ELECTROCHEMICAL PREPARATION OF TRIFLUOROACETIC ACID, SODIUM URANIUM (IV) FLUORIDES, AND URANIUM

By

DONALD RAE ALLEN

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CHAPTER I.

INTRODUCTION

Three new electrochemical syntheses are reported in this dissertation. Each of the three requires an electrochemical reaction as a step in its synthesis.

The first synthesis reported is the novel preparation of trifluoroacetic acid from CF_3CH_3. A high voltage alternating current electric discharge is used to effect the oxidation step. Trifluoroacetic acid has been previously prepared in several different ways. The first reported synthesis of trifluoroacetic acid was by F. Swarts in the year 1922.(19) Swarts oxidized m-trifluoromethyl aniline in chromic acid and obtained trifluoroacetic acid from the reaction. Later Benning and Park demonstrated that 1,1,1-trichloro-2,2,2-trifluoroethane could be converted to trifluoroacetic acid.(3) Henne, Alderson, and Newman discovered that 1,1,2-trichloro-3,3,3-trifluoropropene could be hydrolyzed and oxidized with potassium permanganate in potassium hydroxide solution to yield trifluoroacetic acid.(11) Simons, Pearlson, Brice, Wilson, and Dresdner have demonstrated that acetonitrile can be electrochemically fluorinated in hydrogen fluoride and the resultant trifluoroacetonitrile can be hydrolyzed to yield trifluoroacetic acid.(15)

The molecule 1,1,1-trifluoroethane has three hydrogen atoms attached to one of its carbons and three fluorine atoms attached to its other carbon. It was decided that the oxidation of this molecule should be investigated to determine if it were possible to prepare trifluoroacetic acid from it.

$$2\ CF_3CH_3 + 3\ O_2 = 2\ CF_3CO_2H + 2\ H_2O$$

The compound 1,1,1-trifluoroethane has been reported to be highly resistant to chemical oxidation.(10) This earlier report states that CF_3CH_3 resists oxidation by hot, fuming, nitric acid. Rather than search for a more powerful chemical oxidizer than hot, fuming, nitric acid, an electrochemical oxidation method was chosen. Trifluoroethane and dry air were reacted together in a high voltage alternating current silent electric discharge. The silent electric discharge was produced in an ozonizer powered by an electric transformer. Considerable decomposition of the 1,1,1-trifluoroethane was noted but no trifluoroacetic acid was produced. It was then discovered that by passing a gaseous mixture of trifluoroethane, air, and water vapor through the high voltage discharge, trifluoroacetic acid was the only organic reaction product. Thus, 1,1,1-trifluoroethane was oxidized to trifluoroacetic acid in a single reaction step.

The second synthesis reported in this dissertation is of sodium uranium (IV) fluorides. The product is a mixture of double salts of sodium fluoride and uranium tetrafluoride and has a final elemental analysis approaching $NaUF_5$.

Uranium tetrafluoride is known to form stable double salts with sodium fluoride. C. J. Barton, et al. have published a detailed study of the phase behavior of the NaF-UF_4 system.(2) They accomplished their phase study work by fusing various quantities of sodium fluoride with uranium tetrafluoride and then identifying the forms produced.

A report of the Atomic Energy Commission describes a process, carried out in aqueous solutions, which produces a product described as $NaUF_5$.(1) The $NaUF_5$ product from that process is a mixture of sodium fluoride and uranium tetrafluoride double salts. The report by the Atomic Energy Commission was of value because it showed a method by which uranium tetrafluoride, in the form of salts with sodium fluoride, could be prepared in aqueous solutions. Further, that salt mixture product was readily removed from its mother liquor by filtration and easily dried without loss of its combined fluorine.

Uranium tetrafluoride is ordinarily produced by the reaction of uranium dioxide with anhydrous hydrogen fluoride at temperatures of the order of 400°C..(16)

$$UO_2 + 4\ HF = UF_4 + 2\ H_2O$$

Uranium tetrafluoride hydrate, $UF_4 \cdot 2\frac{1}{2}H_2O$, can be prepared from reactions in aqueous solutions. This hydrate loses a considerable portion of its fluoride content during thermal desiccation.(16) Hence, uranium tetrafluoride prepared from aqueous reactions is of no interest to those requiring a dry or a pure material.

The sodium uranium (IV) fluorides product which the Atomic Energy Commission had prepared could be readily dried at 110°C. without loss of its combined fluorine. But their sodium uranium (IV) fluorides product was contaminated by other metal salts, such as iron salts. The A.E.C. had produced their sodium uranium (IV) fluorides product by the treatment of uranyl nitrate solutions with solutions of ferrous chloride. The ferrous ion, Fe^{+2}, the hexavalent uranium atom of the uranyl ion, and the nitric acid of the solution permit the uranium to be reduced to its tetravalent state.

$$U^{+6} + 2\ Fe^{+2} = U^{+4} + 2\ Fe^{+3}$$

After the hexavalent uranium atoms had been reduced to the tetravalent state, sodium chloride and hydrofluoric acid were added to the system. After the sodium chloride and the hydrofluoric acid had been mixed into the solution, the sodium uranium (IV) fluorides product precipitated and was removed from the mother liquor by filtration. The sodium uranium (IV) fluorides product was found to contain not only iron salts as a contaminant, but the product also contained all of the other metal contaminants which had been in the original uranyl nitrate solution.(1)

In order to improve the purity of the sodium uranium (IV) fluorides product, a new synthesis was devised. The new synthesis is reported in this dissertation. Instead of starting with uranyl nitrate solutions, uranyl chloride was chosen as the starting material. Hydrochloric acid was used as the acid for the system instead of nitric acid. These changes were made in the anion content of the system because an electrochemical reduction of the uranyl ion was planned to be substituted for the chemical reduction step employed by the A.E.C.. Electrochemical reduction of the uranium atoms in the solution would eliminate contamination of the final product with iron salts. In order to be useful in this synthesis, the electrochemical reduction device would have to be capable of quantitatively reducing the uranium in the electrolyte. If the reduction were not quantitative, it would be difficult to remove all of the uranium from the solution. This would pose a problem of health and safety. A special electrochemical cell was designed to accomplish the required quantitative reduction. It employed a horizontally positioned porous carbon cathode and a perforated carbon anode. The electrochemical cell was not only capable of carrying out the reduction efficiently, it was also capable of operating continuously. Instead of using sodium chloride and hydrofluoric acid to prepare the sodium uranium (IV) fluorides product, sodium fluoride was used. The combination of sodium fluoride and hydrochloric acid is a milder fluoridating agent than hydrofluoric acid. Thus, uranyl chloride in hydrochloric acid solution, was electrochemically reduced, treated with sodium fluoride powder, and the sodium uranium (IV) fluorides product precipitated from solution. The chemical reactions which take place in the process may be written as follows:

$$UO_2Cl_2 + 4\,HCl + 2\,F^* = U^{+4} + 4\,Cl^- + 2\,H_2O + Cl_2$$

F* = Faraday

$$U^{+4} + 4\,Cl^- + 5\,NaF = NaUF_5 + 4\,Na^+ + 4\,Cl^-$$

The product, $NaUF_5$, dried at 110°C., was powdered and analyzed. Analysis showed it had an elemental composition approaching that of $NaUF_5$. Spectroscopic examination of the product showed it to be almost entirely free of any elements other than sodium, uranium, and fluorine. Because of the high purity of the product made by this new synthesis, it could be used directly in the preparation of high purity uranium metal. Those contaminants which were introduced into the system with the original uranyl chloride, did not precipitate from the mother liquor and thus did not appear in the final sodium uranium (IV) fluorides product.

The third and last electrochemical synthesis reported in this dissertation is the preparation of uranium metal. In this synthesis, uranium metal is deposited from a fused salt electrolyte which contained uranium tetrafluoride. The fused salt electrolyte is reduced in an electrochemical cell which employs an anode of sodium metal.

Uranium metal was first isolated by E. M. Peligot in 1842.(17) Today there are several methods for preparing uranium metal. The metal has been produced by the electrochemical reduction of a fused salt electrolyte composed of uranium tetrafluoride, potassium fluoride, sodium chloride, and calcium chloride.(17) But the uranium metal used for the manufacture of nuclear fuel elements is usually produced by the reduction of uranium tetrafluoride in a closed vessel at high temperatures.(13) The uranium tetrafluoride is reduced in that vessel by magnesium.

$$UF_4 + 2\ Mg = U + 2\ MgF_2$$

The magnesium reduction reaction is able to produce a pure uranium metal more conveniently than the previously known electrochemical methods.

It was decided to investigate the reduction of uranium tetrafluoride with sodium metal after a thermodynamic study showed that the reaction:

$$4\ Na + UF_4 = U + 4\ NaF$$

should be spontaneous up to temperatures of the order of 2,000°K.. A search of the literature showed that no one had reported the successful reduction of uranium tetrafluoride to uranium metal with sodium. In order to study the proposed sodium reduction reaction under carefully controlled experimental conditions, an electrochemical cell was designed for the purpose, a cell which would allow the sodium metal reactant to become an anode during reaction. This electrochemical cell permitted the reaction to be carried out in an open vessel at atmospheric pressures. Because of the high temperatures at which the cell was operated, it was necessary to surround the operating electrochemical cell with an inert gaseous atmosphere. The cell was visible during operation through windows in the box which covered the cell. Contrary to the calculated spontaneity of the reaction between sodium metal and uranium tetrafluoride, it was found that in order to produce uranium at measureable rates it was necessary to pass an electric current through the system. The sodium metal anode was consumed during this electrochemical operation. Comparison of the quantity of uranium metal produced with the amount of electric current passed through the cell demonstrated that the reactions taking place were electrochemical in nature and not reactions catalyzed by an electric current.

Although the reduction of uranium tetrafluoride to uranium by means of sodium was not measureably spontaneous it could be accomplished and controlled by means of an electric current. Further, it could be carried out at atmospheric pressure. By means of the technique described in this dissertation, sodium metal can now be used to prepare uranium from uranium tetrafluoride.

CHAPTER II.

PREPARATION OF TRIFLUOROACETIC ACID

A. INTRODUCTION

1,1,1-trifluoroethane is known to be highly resistant to chemical attack, it even survives contact with hot fuming nitric acid without decomposition.(10) To oxidize the compound and prepare trifluoroacetic acid it was decided that an electrochemical oxidation might succeed. The reaction to be accomplished was:

$$2\ CF_3CH_3 + 3\ O_2 = 2\ CF_3CO_2H + 2\ H_2O$$

One of the simplest methods of electrically enhancing the chemical reactivity of oxygen is by means of a silent electric discharge of the type used to prepare ozone.(9) Ozonizers of the configuration shown in Figure 1 have been used by many investigators for the purpose of studying chemical reactions.(9)

Air was used as the source of oxygen for these experiments. The initial tests in the silent electric discharge employed gaseous mixtures of dry air and

1,1,1-trifluoroethane. But no trifluoroacetic acid was formed in these initial tests and there was extensive decomposition of the trifluoroethane. It was then discovered that addition of water vapor to the operating system radically changed the outcome of the experiments. Passage of a gaseous mixture of 1,1,1-trifluoroethane, air, and water vapor through the silent electric discharge did produce trifluoroacetic acid. When sufficient quantities of water vapor were added to the reaction, trifluoroacetic acid and water were the only reaction products. Any trifluoroethane which did not react to form trifluoroacetic acid could be recovered.

A series of experiments were conducted to investigate this reaction. Table 1 summarizes the experimental findings of this work.

B. EXPERIMENTAL

1. Materials. The 1,1,1-trifluoroethane used for this study was prepared by the Dow Chemical Company. The water used as a reagent, was distilled to remove impurities. The air was obtained from a compressed air line in the laboratory. The air was purified by passing it through a trap containing 30 per cent sodium hydroxide solution to remove carbon dioxide, and through a Pyrex glass cold trap externally refrigerated with a Dry-Ice and acetone mixture in order to remove water vapor from the air. All air used in this work was so purified prior to use.

2. Apparatus. The reactor for the system is shown in Figure 1 and was fabricated of Pyrex glass. The reactor's electrodes were aluminum foil. The electric power used to create the high voltage alternating current electric discharge was furnished by a transformer (Jefferson or Acme) capable of supplying 15,000 v. ac at 450 va and requiring a primary voltage of 110 ac. The humidifier for the reactant stream was built of 75 mm standard wall Pyrex glass tubing 12 inches in length and closed at each end by means of rubber stoppers through which holes were bored. Tubes were inserted through these holes to allow the injection and the withdrawal of reactants. The humidifier tube itself was loosely packed with broken glass tubing.

The purpose of the tubing was to provide a large surface from which the injected water could readily evaporate.

The reactor and the humidifier were placed in separate insulated boxes for purposes of independent temperature control. Fenwal Thermoswitches were installed in each box for temperature regulation. Nichrome wire electric heaters were installed in each box for heat supply. Electric fan blowers were mounted in each box for circulation of warm air. In experimental use, the humidifier and the reactor were positioned as close to one another as practical. The Pyrex glass tube leading from the humidifier to the reactor was insulated with Pyrex glass wool and cloth tape. To check the temperature of the gaseous mixtures being injected into the reactor, a Pyrex glass tee-joint with a ground glass fitting was installed on that tubing line and a thermometer was fitted into the ground glass joint.

Air and 1,1,1-trifluoroethane were metered into the humidifier through separate Rotameters. Calculations of the quantities of air and trifluoroethane being injected into the system were based on the ambient temperatures of the laboratory. Figure 2 is a description of the flow of reactants as well as a description of the relative positions of the various units of the apparatus. Several different means of collecting the effluent vapor and liquid droplet streams coming from the reactor were employed. At the initiation of the experimental work, a series of three glass cold traps chilled in liquid nitrogen were used to capture all of the effluents. After analytical results showed that under several reaction conditions, there was no product degradation or degradation of unreacted trifluoroethane, a simple water sparger was used for collection of the trifluoroacetic acid product.

3. Analytical Methods. The identification of the trifluoroacetic acid reaction product was done by the Dow Chemical Company using infra-red spectroscopy. For the quantitative experimental results contained in Table 1, the trifluoroacetic acid scrubbed from the effluent stream by means of the distilled water in the water scrubber was analyzed by a 0.1 normal sodium hydroxide titration. The absence of carbon dioxide in the scrubbed product was insured prior to titrations by treatment of the sample to be analyzed with dilute sulfuric acid. Phenolphthalein indicator was used to show the titrations' end points.

4. Experimental Results. A summary of the experimental conditions used and their results is contained in Table 1.

Figure 1.

Reactor used to prepare trifluoroacetic acid

A. Port of entry for gaseous mixture of air, 1,1,1-trifluoroethane, and water vapor

B. Reactor vessel in the shape of a Dewar flask and constructed of Pyrex glass tubing

C. Aluminum foil electrodes

D. Electrical leads to power transformer

F. Exit port for reactants leaving system

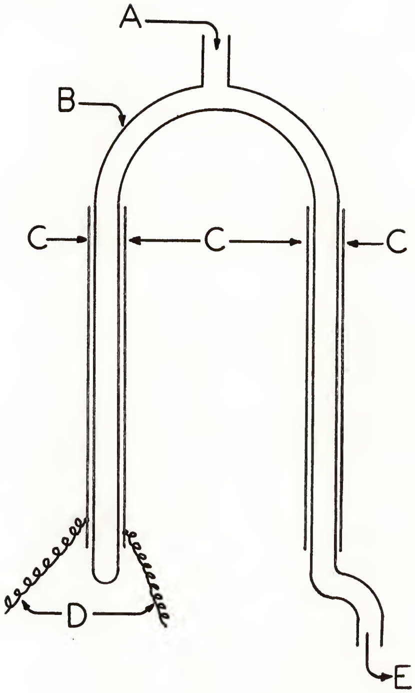

Figure 1.

Figure 2.

Flow sheet for trifluoroacetic acid process

A.	Port of entry for air into system
B.	Rotameter for measurement of air flow
C.	Port of entry for 1,1,1-trifluoroethane into system
D.	Rotameter for measurement of trifluoroethane flow
E.	Recycle path for water. Water used to humidify the gaseous mixture of air and trifluoroethane
F.	Humidifier
G.	High voltage alternating current silent electric discharge reactor
H.	Electrical leads to electric power transformer
I.	Port of exit for vapors and liquids leaving system

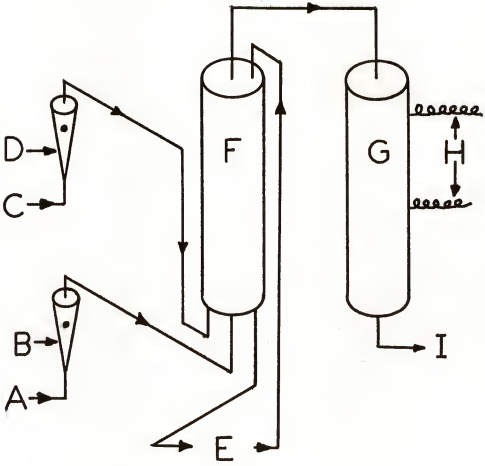

Figure 2.

Table 1.

EXPERIMENTAL RESULTS TRIFLUCROACETIC ACID PREPARATION

	Run Number							
	A	B	C	D	E	F	G	H
Annular spacing, mm.	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Electrode area, cm.^{2}	610	610	610	610	610	610	610	610
Mole ratio, air:MF^a	8	12	14	12	10	12	10	12
Residence time, min.	1.0	1.0	1.0	1.5	1.0	1.3	1.0	2.0
Reactor temperature°	75	75	75	75	75	75	30	75
Air rate, cc./min.	139	145	146	96	142	42	164	72
MF^a rate, cc./min.	17.3	12.0	10.5	8.0	14.3	3.5	16.4	6.0
Total operating time, min.	120	120	120	120	120	120	30	120
% H_2O saturation at 30°	100	100	100	100	100	100	100	0
Total MF^a passed, g.	7.01	4.87	4.26	3.25	5.84	1.42	1.65	2.07
TFA^b produced, g.	2.286	2.078	1.222	1.536	1.935	0.949	0.268	None
TFA^b theory, g.	9.52	6.61	5.78	4.41	7.93	1.93	2.25	MF^a decomp.
% Yield per pass	24.0	31.5	21.2	34.8	24.5	49.2	11.9	H_2SiF_6 in trap

	Run Number							
	I	J	K	L	M	N	O	P
Annular spacing, mm.	3.0	5.5	3.0	3.0	3.0	3.0	3.0	3.0
Electrode Area c.m.^{2}	610	610	305	610	610	610	610	610
Mole ratio, air:MF^a	10	10	10	10	10	10	10	12
Residence time, min.	1.0	1.0	1.0	1.0	1.0	1.0	2.0	2.0
Reactor temperature°	30	45	45	45	75	75	75	75
Air rate, cc./min.	327	260	156	156	142	142	72	72
MF^a rate, cc./min.	33	26	16	16	14	14	6.0	6.0
Total operating time, min.	30	150	150	300	150	300	120	120
% H_2O saturation at 30°	100	100	100	100	100	100	50	50
Total MF^a passed, g.	3.30	13.18	8.01	16.02	7.30	14.60	2.44	2.44
TFA^b produced, g.	0.194	1.570	0.660	2.210	2.001	3.243	Traces of TFA^b	
TFA^b theory, g.	4.50	17.88	10.86	21.72	9.91	19.82	considerable H_2SiF_6	
% Yield per pass	4.3	8.8	6.1	10.2	20.2	16.4		

^{a} 1,1,1-Trifluoroethane. ^{b} Trifluoroacetic acid.

C. DISCUSSION OF EXPERIMENTAL RESULTS

The experiments reported in Table 1 demonstrate that 1,1,1-trifluoroethane can be oxidized to trifluoroacetic acid in a single step electrochemical reaction. The equation for the reaction cannot be written as:

$$2\ CF_3CH_3 + 3O_2 + S.E.D.^* = 2\ CF_3CO_2H + 2\ H_2O$$

S.E.D.* = silent electric discharge

Water vapor was an essential reactant. If water vapor is included in the equation it becomes:

$$2\ CF_3CH_3 + 3O_2 + x\ H_2O + S.E.D.^* = 2\ CF_3CO_2H + y\ H_2O$$

But the exact mechanism of the oxidation of the trifluoroethane is not known in the experiments reported. It is known that when water vapor is added to the mixture of trifluoroethane and air that trifluoroacetic acid is the only organic reaction product and further that any trifluoroethane which did not form the acid could be recovered. Further, no ozone was detected in the gaseous exhaust stream coming from the reactor.

Since water vapor has been demonstrated to be essential to the formation of trifluoroacetic acid in these experiments, it is possible that the actual oxidizer of the trifluoroethane is derived from water. Lavin and Stewart have shown the occurance of the hydroxyl radical, OH• , in electric discharges through water vapor.

They noted that the hydroxyl radicals have relatively long lives after formation in an electric discharge and could be detected up to distances as great as 350 mm. from their point of formation.(14) The hydroxyl radical is thought to be stabilized by the presence of oxygen. (18) And, the hydroxyl radical has been shown to be more reactive than atomic oxygen.(12) Jackson was able to cause the hydroxyl radical to oxidize carbon monoxide to carbon dioxide.(12)

It is suggested that future work on this trifluoroethane reaction be directed towards establishing the mechanism of the oxidation. The same experimental apparatus which has been used in the initial work is suitable for future experiments. However, instead of starting with the trifluoroethane, air, and water vapor mixture, a simpler system should be used. Start with a gaseous mixture of trifluoroethane and water vapor. Then, after investigating this two component system, add pure oxygen to the reactants stream and observe the changes. Small quantities of pure oxygen should be used at the start of such work and increasing amounts later as needed.

CHAPTER III.

PREPARATION OF SODIUM URANIUM (IV) FLUORIDES

A. INTRODUCTION

Uranium tetrafluoride is the chemical intermediate frequently used to prepare uranium metal.(13) Uranium tetrafluoride can be produced by reaction of uranium dioxide with hydrofluoric acid.

$$UO_2 + 4\ HF = UF_4 + 2\ H_2O.$$

The uranium tetrafluoride prepared in this manner is hydrated, $UF_4 \cdot 2\frac{1}{2}H_2O$, and it loses a considerable portion of its fluorine during thermal desiccation.(16) In order to prepare anhydrous uranium tetrafluoride which is suitable for the manufacture of pure uranium, it is necessary to react pure uranium dioxide with anhydrous hydrogen fluoride at temperatures of about 400°C..(16)

A report by the Atomic Energy Commission described a process by which it was claimed that a sodium uranium (IV) fluoride product was obtained which had a chemical composition corresponding to $NaUF_5$.(1) This reported process was carried out in aqueous solutions. The $NaUF_5$ product was readily separated by filtration and did not lose its fluorine on drying at 110°C.. But their $NaUF_5$ product was contaminated with salts of metals other than uranium and so could not be used in the preparation of pure uranium metal. The A.E.C. did not structurally identify the product which they called $NaUF_5$. The product is actually a mixture of double salts of sodium fluoride and uranium tetrafluoride. C. Barton, et al. later demonstrated that sodium fluoride and uranium tetrafluoride react together to produce a series of double salts without evidence of the complex ion, UF_5^-, implied by the formula used above.(2) Figure 3 is a phase diagram of the NaF-UF_4 system.(2) The fact that the product obtained from this mixture is a uranium tetrafluoride is the most important consideration. The value of the A.E.C.'s report was not diminished because the product was a mixture of double salts rather than a single species. The mixture of double salts product could be readily dried without fluorine loss and this was valuable information.

In order to prepare this mixture of sodium uranium (IV) fluorides product from reactions taking place in aqueous solutions, and have that product free of other contaminants was the object of this study. In order to accomplish this objective, a new synthesis was developed and is reported here. The A.E.C. had taken

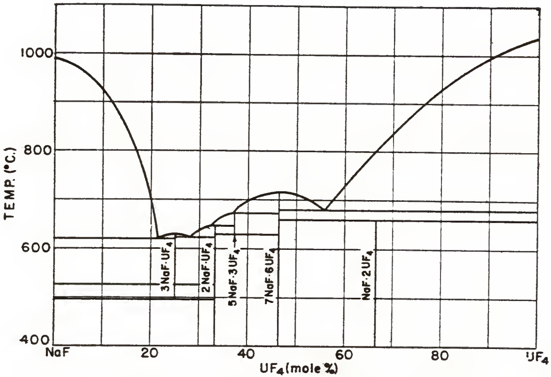

Figure 3. The System NaF-UF$_4$ (Ref. 2.)

uranyl nitrate, $UO_2(NO_3)_2$, in dilute nitric acid as its starting material. The hexavalent uranium atoms were reduced to the tetravalent state by treatment of the above solution with a solution of ferrous chloride.

$$U^{+6} + 2\ Fe^{+2} = U^{+4} + 2\ Fe^{+3}$$

The tetravalent uranium was then precipitated from solution by addition of sodium chloride and hydrofluoric acid. Their $NaUF_5$ product immediately precipitated and was removed by filtration, washed, and dried in a warm air oven. Their final product was found to be free of water and no fluorine losses were noted during desiccation. The author decided that a pure sodium uranium (IV) fluorides product might be made from reactions taking place in aqueous solutions if an electrochemical reduction of the uranium were possible. To simplify the handling of the aqueous solutions and to make the electrochemical reduction easier, it was decided to use a chloride system instead of the nitrate system of the A.E.C.. A special electrochemical cell was developed for the uranium reduction because that reduction step had to be quantitative with respect to the uranium ions. If the reduction step were not quantitative it would be difficult to prevent loss of uranium salts. The electrochemical cell features a horizontally positioned porous carbon cathode and a horizontally positioned perforated carbon anode. This combination of design features not only allows the hexavalent uranium to be quantitatively reduced, but allows this reduction to take place continuously. Starting with a solution of uranyl chloride, UO_2Cl_2, in hydrochloric acid, HCl, the electrochemical reduction reaction converts the hexavalent uranium to tetravalent uranium ions at the operating porous carbon cathode. Chlorine gas is generated at the perforated carbon anode. The electrochemical reaction can be written as:

$$UO_2Cl_2 + 4\,HCl + 2F^* = U^{+4} + 4\,Cl^- + 2\,H_2O + Cl_2$$

F^* = Faraday

Because hydrochloric acid was used in this reaction and small amounts would remain in the mother liquor from the excess acid actually employed, there was no need to use hydrofluoric acid as the source of the fluoride ion. Sodium fluoride itself would be a satisfactory fluoridating agent. The product precipitation reaction can then be written as:

$$U^{+4} + 4\,Cl^- + 5\,NaF = NaUF_5 + 4\,Na^+ + 4\,Cl^-$$

The reaction takes place smoothly in the acid medium provided by the hydrochloric acid. The sodium uranium (IV) fluorides products prepared by the process described in the experimental section of this chapter are of very high purity and may be used directly in the preparation of pure uranium metal.

B. EXPERIMENTAL

1. Materials. The uranium oxide which was used as the source of all uranium values in this work was taken from a mill sample Lot (550) 274. This uranium oxide sample was spectroscopically analyzed and found to contain 54 per cent uranium, plus iron, sodium, copper, vanadium, aluminum, silicon, and tungsten as impurities. The sodium fluoride and the hydrochloric acid were laboratory reagent grade materials.

2. Apparatus. All Pyrex glass vessels used in this work were cleaned with dilute hydrochloric acid, 3 per cent, prior to use. The acid wash was to insure that all acid soluble materials had been leached from the glassware and would not find their way into the final product. The electrochemical cell used for the reduction of the uranium had a porous carbon cathode, Grade 40 porous carbon from the National Carbon Company. The anode was a plate of impervious carbon and is described in Figure 5. The anode and cathode connections were graphite rods. Figure 4 describes the porous carbon cathode and shows the graphite rod connectors. Figure 5 shows the assembly of the anode. Figure 6 is a cross section of the assembled electrochemical cell. The cell's body was of glass tubing and had

three holes to permit insertion of the graphite rods into the porous carbon cathode. The porous carbon cathode was sealed to the inner wall of the glass cell body by means of Apiezon wax. The wax prevented leakage of the cell's electrolyte at the interface of the porous carbon and the glass body's inner wall. By sealing the porous carbon cathode to the body wall, all fluids admitted to the cell had to pass through the operating cathode prior to leaving the system. In order to insure that the anode and cathode were relatively free of organic compounds (tars) the assembled electrochemical cell was initially operated for a period of four hours with an electrolyte of dilute, 5 per cent, hydrochloric acid. While the dilute hydrochloric acid was slowly being passed through the cell, an electric current was passed through that cell. The voltage of the current was just sufficient to cause generation of hydrogen gas at the cathode and chlorine gas at the anode. A liquid flow rate of 2 liters per hour was used during the cleaning operation. When the porous cathode cell had been thus cleansed, it was ready for use in the reduction of uranium salt solutions.

Pyrex glass vessels were used for fluoridation of the solutions containing the uranous ion. The solution was stirred during the precipitation by a laboratory stirrer equipped with a Pyrex glass impeller. The product sodium uranium(IV) fluorides obtained from these reactions was dried in Pyrex glass beakers at 110°C. in a laboratory warm air oven. Although Pyrex glass was extensively used in these experiments, there was no noticeable etching of the glass.

3. Analytical Methods. The starting material, a mill sample of uranium oxide was analyzed by emission spectroscopy. The uranyl chloride solution used for these tests was prepared from that sample. The uranyl concentration in the starting solutions was determined by reduction in a Jones reductor followed by titration of the sample with potassium permanganate. The uranous concentration of the product from the porous cathode electrochemical cell was titrated with a standardized potassium permanganate solution. The uranium content of the final sodium uranium (IV) fluorides product was determined by emission spectroscopy, the sodium content by flame photometry, and the fluoride content by volatilization of the fluoride content as hydrofluosilicic acid and titration of this acid by sodium hydroxide solution. These analyses were performed by the Dow Chemical Company.

4. Experimental Results. Table 2 is an operation summary of the electrochemical reduction of the uranyl chloride solutions employed in this study. This summary

includes a fractional factorial experimental design to calculate the approach toward optimum reaction conditions. This design is based on the method of Box and Wilson.(4) The design itself is a two-level three-variable half replica. A sample calculation, based on information contained in Table 2 is included in the appendix of this dissertation. For further information on the use of factorial designs, the reader is referred to a text on the subject of experimental design authored by O.L. Davies.(5)

The uranous chloride in hydrochloric acid solution produced by the porous carbon cathode electrochemical cell was treated with sodium fluoride powder. The product sodium uranium (IV) fluorides immediately precipitated. Table 3 is an optimization study for this reaction. The reaction is:

$$U^{+4} + 4\,Cl^{-} + 5\,NaF = NaUF_5 + 4\,Na^{+} + 4\,Cl^{-}.$$

Table 3 notes the time required for mixing in the sodium fluoride powder, and also notes the interval between the completion of NaF addition and the first filtration, called the "buildup time". After the first filtration, the filtrate was permitted to stand at room temperatures (referred to as "settling time") and then refiltered. The amount of product sodium uranium (IV) fluoride product recovered on the first filtration, as a per cent of that which the solution contained is recorded in Table 3 as "Recovery A". Likewise for the percentages recorded for "Recovery B" from the second filtration. The sodium uranium (IV) fluorides product readily filtered. After the precipitates had been washed and dried, they were found to have a typical composition of:

Uranium	65.4 per cent
Sodium	6.7 per cent
Fluoride	26.5 per cent
Calcium	less than 100 parts per million
Aluminum	less than 100 parts per million

with no iron, vanadium, silicon, copper, or tungsten detectable in the products.

Figure 4.

Porous carbon cathode used in electrochemical cell

I. Side View

   A. Porous carbon cathode's effective face

   B. Hole drilled into body of porous carbon to permit insertion of graphite connector rods

   C. Porous carbon body of cathode made of Grade 40 Porous Carbon, 1 inch thick, 4½ inches in diameter

II. Top View of cathode

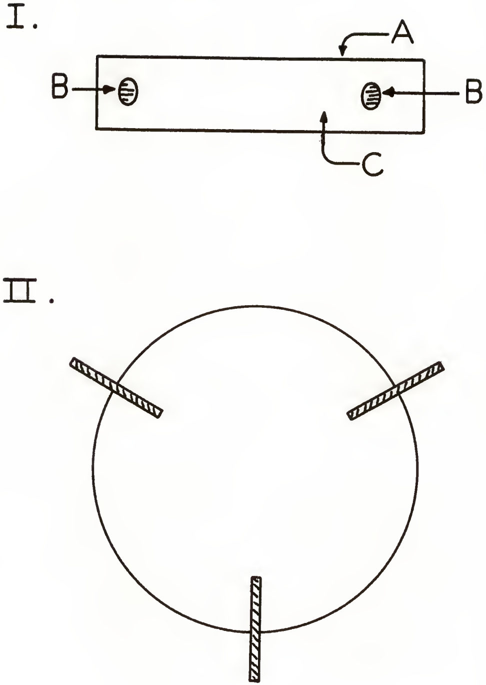

Figure 4.

Figure 5.

Impervious carbon anode used in electrochemical cell

I. Side View

  A. Graphite connector rod, diameter ½ inch and length of 12 inches. This connector rod was attached to the anode disk (B) by means of a tie pin inserted through both the anode disk and the connector rod.

  B. Impervious carbon disk

  C. Connector pin used to securely attach the rod and disk together

II. Underside View

  A. Anode disk of impervious carbon 1 inch thick 4 inches in diameter

  B. Vent holes bored through disk to allow escape of chlorine gas generated during electrolysis

  C. Bottom of graphite connector rod

  D. Graphite pin one-eigth inch in diameter positioned to firmly attach rod and disk

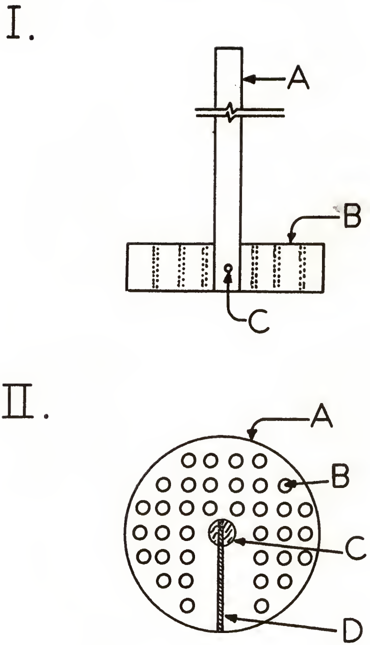

Figure 5.

Figure 6.

Porous carbon cathode electrochemical cell, Side View

A. Anode rod
B. Cell body of Pyrex glass
C. Porous carbon cathode
D. Connector rod for cathode
E. Exit port for cathode compartment

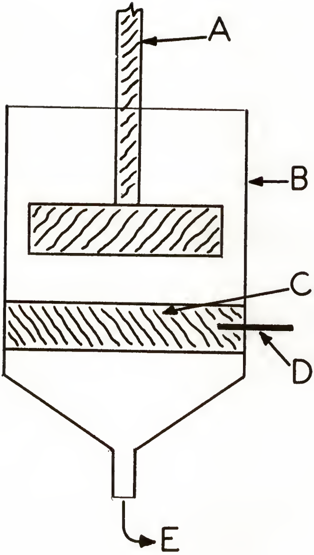

Figure 6.

Figure 7.

Arrangement of laboratory apparatus for electrochemical reduction

A. Gravity feed bottle for stock solution of uranyl chloride in hydrochloric acid solution

B. Stock solution of UO_2Cl_2 in HCl

C. Anode

D. Pyrex glass cell body

E. Cathode

F. Valve for control of flow rate of catholyte from cell

G. Rotameter for measurement of catholyte flow

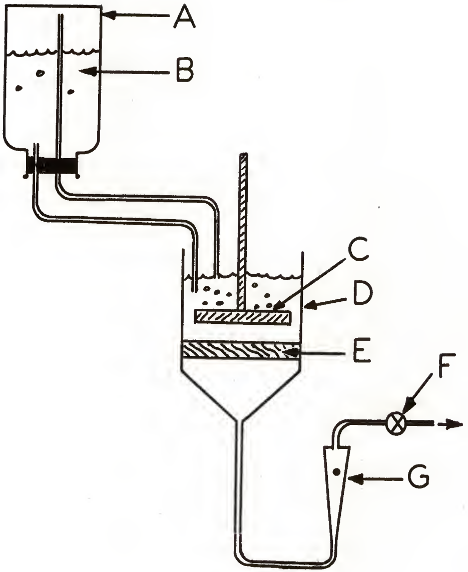

Figure 7.

Table 2. OPERATION SUMMARY FOR POROUS CATHODE CELL

Run No.	U. conc. (g. per liter)	HCl / UO_2Cl_2 Moles/ mole	HCl conc. (%)	Current (ampr.)	Conversion %	Current Eff. %	Volt.
a	30.0	10:1	4.4	0.7	88.3	66.4	1.7
b	46.0	20:1	14.0	1.1	78.7	51.2	1.3
c	49.5	10:1	7.3	1.1	92.0	79.4	1.3
d	28.8	20:1	8.8	1.0	65.9	57.2	1.3
e	34.6	22:1	11.0	3.3	100.0	72.0	2.5
f	42.1	35:1	18.7	2.0	92.0	72.0	1.3
g	50.8	9:1	7.0	1.5	98.3	90.0	1.3

Factorial Summary *

Factor	Levels		
	Low	High	Optimum
U. conc.-gms./liter	30	50	188
HCl/UO_2Cl_2 - moles/mole	10	20	4
Residence time - min./gm.	5.0	6.42	2.75

* Based on a,b,c,d.

Table 3. OPTIMIZATION STUDY FOR SODIUM URANIUM (IV) FLUORIDES PRECIPITATION

Factor	Unit	Run Levels abcd	abe	ace	ad	bc	bde	cde	I
Uranous ion	gms./liter	40	40	40	40	20	20	20	20
HCl/UCl_4	moles/mole	20	20	17	17	20	20	17	17
NaF	% excess	15	5	15	5	15	5	15	5
Mixing time	minutes	6	2	2	6	2	6	6	2
Buildup time	minutes	8	16	16	8	8	16	16	8
Recovery A	per cent	97.8	95.0	98.5	97.8	96.3	95.2	98.6	91.0
Recovery B	per cent	94.8	90.3	98.1	94.8	94.3	89.3	98.2	93.3
Settling time for Recovery B	minutes	64	250	85	81	117	98	45	300

Factorial Summary

Factor	Low	High	Optimum A	Optimum B	Optimum C
Uranous ion (g./l.)	20	40	34.0	37.0	30.0
HCl/UCl_4 moles/mole	17	20	18.5	12.7	18.5
NaF per cent excess	5	15	12.1	31.5	10.0
Mixing time minutes	2	6	4.6	4.5	4.0
Buildup time min.	8	16	10.0	10.8	12.0

C. DISCUSSION OF EXPERIMENTAL RESULTS

A mixture of sodium uranium (IV) fluorides has been prepared from reactions taking place in aqueous solutions. By the method of preparation described in this dissertation, that mixture is almost completely free of contaminants. The fact that the product is a mixture of sodium fluoride - uranium tetrafluoride double salts rather than being a single compound, in no-wise enhances or detracts from the utility of the product itself. The product sodium uranium (IV) fluorides mixture may be directly used in the preparation of pure uranium metal. This will be demonstrated in Chapter IV of this dissertation.

The chemical reactions which allowed the preparation of the sodium uranium (IV) fluorides mixture are as follows:

$$UO_2Cl_2 + 4\ HCl + 2F^* = U^{+4} + 4\ Cl^- + 2H_2O + Cl_2$$

F^* = Faraday

$$U^{+4} + 4\ Cl^- + 5\ NaF = NaUF_5 + 4\ Na^+ + 4\ Cl^-.$$

The electrochemical cell, by reason of its design features, permitted the continuous quantitative uranium reduction to take place. When using this cell, the flow rate of electrolyte must be balanced against the current flow through the cell. If an insufficient quantity of electric current is used for a given flow rate of a solution of known uranium content, reduction of the uranium will be incomplete and the cell product will be a mixture of hexavalent uranium and tetravalent uranium. On the other hand, if an excessive amount of current is employed, not only will all of the uranium be reduced to the tetravalent state but also some hydrogen gas will be generated on the cathode. This hydrogen co-product on the cathode will not be injurious to the final reduction result, but it will not serve a useful purpose. Of the two operating conditions, use of too little electric current or use of too much current, it is better to waste a small quantity of electricity and insure that the uranium reduction was complete. Because of its electrode design features, the cell can be operated continuously for an indefinitely long period of time.

The high purity of the product can be attributed to the combination of variable used; the use of a chloride system instead of the nitrate system used by the Atomic Energy Commission; the use of an electrochemical reduction instead of a chemical reduction; and the use of sodium fluoride as the fluoridating agent all contributed to the successful result.

It would be of interest to determine how little sodium fluoride could be used in this synthesis, for a given quantity of uranium and still be able to produce a readily filtered and dried product. At what ratios of reactants does the final filtered products mixture contain hydrated uranium tetrafluoride? The studies reported in this disseration show the manner by which the maximum quantities of uranium can be extracted from the solutions. Later studies should be directed toward determining how little sodium fluoride, per given uranium concentration, can be employed and still precipitate a readily dried product.

CHAPTER IV.

PREPARATION OF URANIUM

A. INTRODUCTION

Uranium metal, particularly the uranium metal used in the construction of nuclear fuel elements, is usually prepared by the reduction of uranium tetrafluoride with magnesium metal. In the case of the reduction of uranium tetrafluoride with magnesium, powdered UF_4 and powdered magnesium are mixed together and this mixture is then tamped into a metal pressure cell or vessel. The vessel is then sealed closed and gradually warmed until the spontaneous reaction:

$$UF_4 + 2\,Mg = U + 2\,MgF_2$$

is initiated. After initiation of reaction, the external temperature of the vessel is then controlled to prevent its melting from the heat generated within. Uranium metal is formed by this reaction and also a co-product, magnesium fluoride. The magnesium fluoride separates from the metal. After the reaction mass has cooled, the vessel is opened and, then, the metal is parted from the salt.(8) (13)

Like magnesium metal, sodium metal can react with uranium tetrahalides. Sodium metal can react with uranium tetrachloride to yield uranium.(13)

$$4\ Na + UCl_4 = U + 4\ NaCl$$

But, the present-day nuclear fuels industry uses uranium tetrafluoride, UF_4, as the intermediate for uranium metal preparation. It was decided to investigate the reduction of uranium tetrafluoride with sodium. An investigation of the literature showed that the successful reduction of uranium tetrafluoride to uranium metal by means of sodium metal had not been reported.

$$4\ Na + UF_4 = U + 4\ NaF$$

A study was then made of the thermodynamics of both reactions, the magnesium reduction of uranium tetrafluoride, and the sodium reduction of uranium tetrafluoride to see how they compared in theory. Table 4 and Table 5, together with Figure 8 express the free energy and the enthalpy changes which are associated with the reduction of uranium tetrafluoride by magnesium. Table 6 and Table 7, together with Figure 9, show the free energy and the enthalpy changes which are associated with the reduction of UF_4 by sodium. Both systems, magnesium and sodium reductions are strikingly similar. The magnesium reduction reaction is spontaneous up to temperatures as high as $2200^{o}K$.. The sodium reduction reaction should be

Table 4.

ENTHALPY CHANGES ASSOCIATED WITH THE REACTION:

$$2\ Mg + UF_4 = U + 2\ MgF_2$$

Temp. °K.	UF_4 ΔH_f K.cal./mole	MgF_2 $2\Delta H_f$ K.cal./mole	ΔH_r K.cal.
300	-443	-526	-83
400	-443	-526	-83
500	-442	-526	-84
600	-441	-526	-85
700	-440	-524	-84
800	-440	-524	-84
900	-439	-524	-85
1000	-439	-528	-89
1100	-439	-528	-89
1200	-438	-526	-88
1300	-437	-526	-89
1400	-430	-588	-158
1500	-432	-586	-154
1600	-431	-556	-125
1700	-372	-548	-176
1800	-373	-554	-181
1900	-373	-552	-179
2000	-373	-550	-177
2100	-373	-548	-175
2200	-373	-546	-173
2300	-376	-544	-188
2400	-379	-544	-185
2500	-379	-412	- 33
2600	-379	-412	- 33
2700	-380	-412	- 32
2800	-380	-412	- 32
2900	-380	-412	- 32

Based on data from reference 6.

Table 5.

FREE ENERGY CHANGES ASSOCIATED WITH THE REACTION:

$$2\ Mg + UF_4 = U + 2\ MgF_2$$

Temp. °K.	UF_4 ΔF_f K.cal./mole	MgF_2 $2\Delta F_f$ K.cal./mole	ΔF_r K.cal.
300	-421	-502	-81
500	-407	-492	-85
700	-393	-468	-75
900	-380	-452	-72
1100	-367	-436	-69
1300	-354	-418	-64
1500	-342	-398	-56
1700	-330	-376	-46
1900	-325	-354	-29
2100	-320	-334	-14
2300	-318	-314	+ 4
2500	-315	-300	+15
2700	-310	-290	+20
2900	-305	-282	+23

Based on data from reference 6.

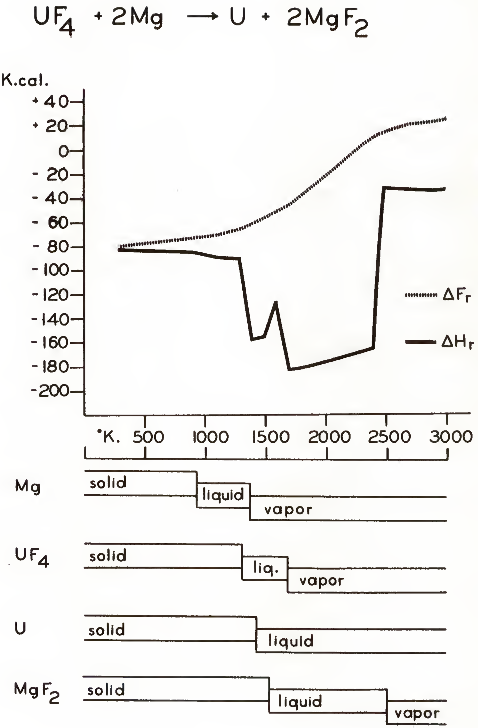

Figure 8. ΔF and ΔH plots for Mg-UF_4

Table 6.

ENTHALPY CHANGES ASSOCIATED WITH THE REACTION:

$$4\ \mathrm{Na} + \mathrm{UF_4} = \mathrm{U} + 4\ \mathrm{NaF}$$

Temp. °K.	UF_4 ΔH_f K.cal./mole	NaF $4\Delta H_f$ K.cal./mole	ΔH_r K.cal.
300	-443	-544	-101
400	-443	-548	-105
500	-442	-548	-106
600	-441	-548	-107
700	-440	-544	-104
800	-440	-544	-104
900	-439	-544	-105
1000	-439	-544	-105
1100	-439	-540	-101
1200	-438	-632	-194
1300	-437	-600	-163
1400	-430	-596	-166
1500	-432	-596	-164
1600	-431	-592	-161
1700	-372	-588	-216
1800	-373	-588	-215
1900	-373	-584	-211
2000	-373	-384	- 11
2100	-373	-384	- 11
2200	-373	-384	- 11
2300	-376	-384	- 8
2400	-379	-384	- 5
2500	-379	-384	- 5
2600	-379	-384	- 5
2700	-380	-384	- 4
2800	-380	-384	- 4
2900	-380	-384	- 4

Based on data from reference 6.

Table 7.

FREE ENERGY CHANGES ASSOCIATED WITH THE REACTION:

$$4\,Na + UF_4 = U + 4\,NaF$$

Temp. °K.	UF_4 ΔF_f K.cal./mole	NaF $4\Delta F_f$ K.cal./mole	ΔF_r K.cal.
300	-421	-516	-95
500	-407	-500	-93
700	-393	-480	-87
900	-380	-460	-80
1100	-367	-444	-77
1300	-354	-416	-62
1500	-342	-388	-46
1700	-330	-360	-30
1900	-325	-332	- 7
2100	-320	-320	0
2300	-318	-312	+ 6
2500	-315	-308	+ 7
2700	-310	-300	+10
2900	-305	-296	+ 9

Based on data from reference 6.

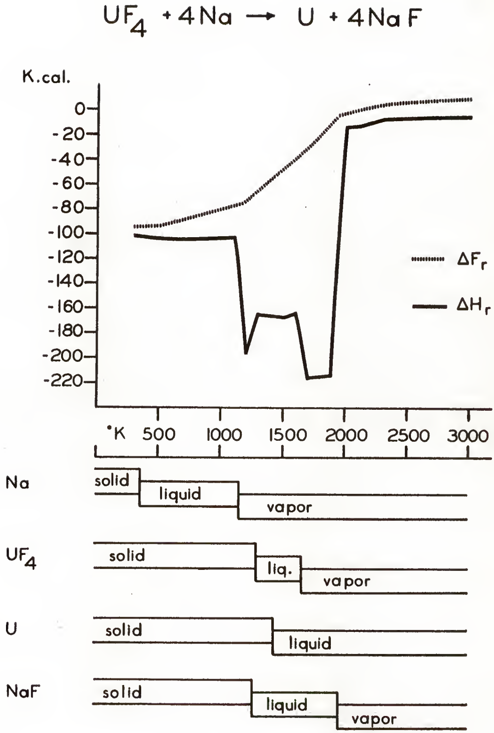

Figure 9. ΔF and ΔH plots for Na-UF_4

spontaneous up to temperatures as high as 2100°K.. The purpose of the laboratory work was to determine if, and under what experimental conditions, sodium metal could be used to prepare uranium from uranium tetrafluoride. Because the reaction had not been reported in the literature, it was thought that it must not take place readily. In the past twenty years a great deal of research work has been done on the chemistry of uranium and rather than use such devices as the vessels used for magnesium reduction, it was decided to try something very different from anything which might have been tried before. An electrochemical cell was designed which had an electrode in the shape of a tube. The purpose of the tube was to provide a means of confining the sodium metal during reaction. The other electrode for the cell was a cup in which the uranium tetrafluoride containing electrolyte could be contained. In operation, a fused salt would be held in the cup electrode and a tube electrode would be immersed in the fused salt. Figure 10 is a side view of the electrochemical cell which was used for the experiments reported in this dissertation. Essentially, it is a cup and tube device. The tube is supported by Vycor rods. These rods rest on the mouth of the container cup and keep the tube from falling to the bottom of the cell. The cell's cup and tube are made of graphite. This cell design permits molten uranium tetrafluoride, in a fused salt system, to be brought into intimate contact with molten sodium. And, if the reaction does not take place spontaneously, an electric current can be passed through the system to assist the reaction. The effective face of the anode of this system is sodium metal because sodium is a more reactive chemical than is graphite. By using this electrochemical approach it was then possible to by-pass the need for vessels to contain the reagents at super-atmospheric pressures.

Because the sodium uranium (IV) fluorides mixture produced by the synthesis reported in the third chapter of this dissertation was highly pure, it was decided to use this mixture as a part of the electrolyte system. In order to lower the temperature of the sodium uranium (IV) fluorides mixture, sodium chloride was also used in the electrolyte system. The electrolyte composition used for this work was 65 per cent sodium uranium (IV) fluorides mixture and 35 per cent sodium chloride. This salt system was fused together in the cathode cup by warming that cup with an externally mounted electric heater. The electric resistance heater was also used during the reaction to maintain the cell at the necessary high temperatures. Both graphite and sodium are sensitive to air when they are heated to high temperatures. It was necessary to protect the cell parts and contents from air attack during the course of the experiments. This was accomplished by placing a box, made of Transite, over the cell and then forcing an inert gas, argon, into the box.The rapid flow of argon displaced the air from the area of the cell and protected the sensitive parts of the system during the experiments.

Uranium has been produced electrochemically prior to the work reported in this dissertation. Driggs and Lilliendahl had accomplished and reported electrochemical reduction of uranium tetrafluoride in 1930.(7) They did not use a sodium anode but rather employed a system in which uranium was deposited against the cathode and chlorine gas was discharged against the anode. Their electrolyte was composed of sodium chloride, calcium chloride, and potassium uranium (IV) fluoride. When uranium was plated out of the system, and chlorine gas was driven out of the system, the available fluoride combined with the available calcium to form calcium fluoride. This calcium fluoride was insoluble in the fused salt electrolyte. After their electrochemical cell had been operated for a short time, the electrolyte was laden with particles of calcium fluoride and could not be used. Because of this and other complication, uranium metal is usually produced by reduction of the uranium tetrafluoride salt with magnesium metal. The electrolyte system used in the experiments shown later in this chapter, does not have the homogeneity limitation associated with the system of Driggs and Lilliendahl. No insoluble fluoride precipitate from the melt during cell operation.

B. EXPERIMENTAL

1. Materials. The sodium uranium (IV) fluorides used in the work reported in this chapter were made by the synthesis which has been reported in Chapter III. The sodium chloride used in the electrolyte and the sodium metal were laboratory reagent grade chemicals.

2. Apparatus. The electrochemical cell design used in the following experiments is shown in Figure 10. The cathode cup and the anode tube are made of electrode grade graphite. The anode tube support rods are of Vycor glass. The assembled cells were heated to reaction temperatures by means of an electric crucible furnace. Electric power for the operation of the electrochemical cells was obtained from a rectifier capable of delivering a maximum of 100 amperes at 20 volts direct current. The rectifier was built at the laboratory. A Weston 0 to 50 ampere direct current ammeter and a 0 to 3 volts direct current voltmeter were used for instrumentation of the operating test cell. The voltmeter and the ammeter were calibrated prior to use. The temperature of the electrochemical cell was measured by means of an iron-constantan thermocouple. Temperature was periodically measured by placing the thermocouple against the body of the cathode cup. Figure 11 is a description of the cell and its

electric circuit. The double-pole double-throw electric switch was used in the circuit to allow electrical measurements to be made prior to, as well as during, the passage of current through the cell. When the switch was in position "1", amperage measurements could be made of the dead short condition across the cell's anode and cathode. When the switch was in position "2", voltage measurements could be made across the cell's electrodes. When the swtich was in position "3", an electric current could be passed through the cell and the voltage and amperage of the system could be measured.

In order to exclude air from the vicinity of the operating cell, the cell and its heater were placed on a table top. The cell unit was then covered by a Transite box. The box was equipped with two glass paned viewing ports and a tubing adapter for attaching the argon supply. The inert argon was used to protect the cell and its contents from air attack during operation. Figure 12 is a description of the box used to cover the cell during operation. The argon gas injected into the box, left the box by way of the separation between the bottom of the box and the table top. A gas flow of approximately one cubic foot per minute was injected into the top of the box. At the end of each experimental run, the cell was permitted to cool to room temperature and broken open.

The uranium metal was found to be deposited on the cathode. The metal was collected and analyzed to determine yield. For each experimental cell run, it was necessary to use a new electrochemical cell.

3. Analytical Methods. The uranium metal produced in these experiments was weighed and then analyzed by emission spectroscopy.

4. Experimental Results. Table 8 summarizes the experimental results of this study. In each case, the electrochemical cells had open circuit voltage of zero. In each case, the electrochemical cells had dead short amperages of zero. When an external electric voltage was applied to a cell, that voltage and its resultant amperage were measureable. The voltages reported in Table 8 and Table 9 are corrected for lead line and apparatus resistance.

In each of the experimental runs reported in Table 8, the electrolyte consisted of 300 grams of a mixture of 65 per cent sodium uranium (IV) fluorides and 35 per cent sodium chloride. The temperature of the electrochemical cell's body was maintained at approximately 1,000°K. for all of the experimental runs.

Figure 10.

Sodium anode electrochemical cell

A. Anode cylinder of graphite. Dimensions: 1.54 inches outer diameter, 1.13 inches inner diameter, 10 inches length. An electrical connection was made to this anode tube by means of a nickel strap placed at the top of the tube. Three holes were bored through the tube wall at spacings of 120 degrees. The holes were used to admit three Vycor support rods. The holes were positioned such that the graphite tube was held approximately 1.0 inch above the floor of the cathode cup. The holes were ¼ inch in diameter.

B. Vycor support rods, three. Dimensions: ¼ inch diameter and 4 inches length. These three rods are inserted into the anode tube holes.

C. Cathode cup of graphite. Dimensions: 3¼ inches outer diameter, 2¼ inches inner diameter, 5 inches length. This body serves as both the system's cathode and the container for the fused salt electrolyte. In operation, the anode "A" with its Vycor support rods "B" is coaxially positioned on the cup's mouth.

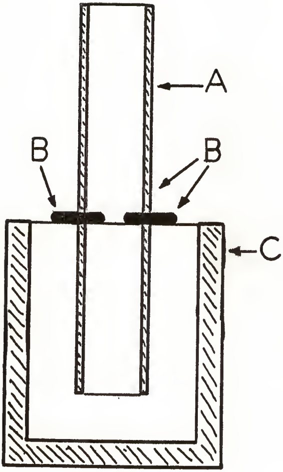

Figure 10.

Figure 11.

Electrical Connections for test cell

A. Leads to direct current rectifier
B. Double pole double throw electric switch
C. Voltmeter
D. Ammeter
E. Test cell

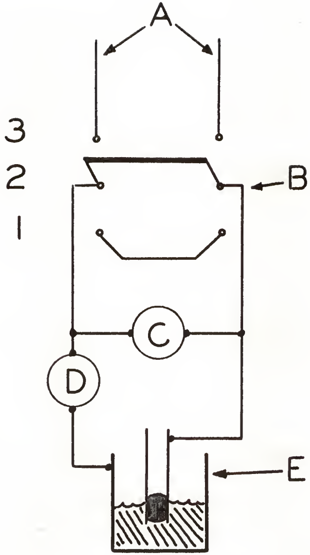

Figure 11.

Figure 12.

Side view of inert gas box

A. Viewing windows, two, glass 5 inches long by 5 inches wide, held in place by means of steel straps

B. Connection for inert gas injection. Made of ¼ inch copper tubing 4 inches long. Copper tubing brazed to a perforated steel plate.

C. Transite box wall. Overall box dimensions: 24 inches long, 24 inches wide, 30 inches high.

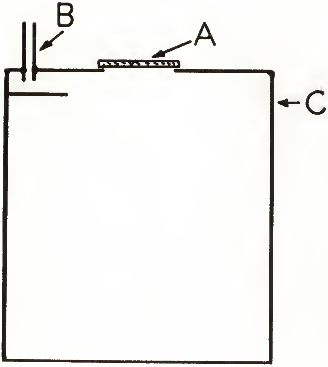

Figure 12.

Table 8.

URANIUM METAL ELECTROCHEMICAL CELL PERFORMANCE

Run No.	Volt. avg.	Amp. avg.	Time min.	U.metal g.prod.	Efficiency per cent *
1.	0.5	32	107	48	38
2.	0.5	26	132	55	43
3.	0.5	24	143	48	38
4.	0.5	30	114	56	44
5.	0.5	30	114	55	43

* Based on actual uranium content of 300 g. of electrolyte

Table 9.

INITIAL AMPERAGE VERSUS VOLTAGE DATA FROM URANIUM METAL ELECTROCHEMICAL CELL RUNS *

Run. No.	Direct current voltage 0.0	0.2	0.3	0.4	0.5	0.6	0.7
1.	0	1	1	2	30	38	44
2.	0	0	1	1	26	32	45
3.	0	1	1	2	24	38	44
4.	0	1	1	2	28	35	40
5.	0	1	1	1	24	36	44

* Same electrochemical cell runs reported in Table 8.

C DISCUSSION OF EXPERIMENTAL RESULTS

No spontaneous reaction was observed to take place between the sodium anode and the uranium tetrafluoride containing electrolyte in the absence of an externally applied electric current. This should not be construed to mean that no spontaneous reaction is possible between the two reactants, but rather that under the experimental conditions employed in this work no such reaction was observed. When an electric potential was applied across the electrodes of the cell, chemical reactions took place and uranium was produced. Thus, the objective of the study was accomplished. It was found that sodium metal could be used to reduce uranium (IV) to uranium. In order to accomplish the reaction at observeable rates, energy in the form of an electric current had to be added to the system. An outgrowth of this research work was an electrochemical cell design which permitted sodium metal to be brought into intimate contact with a fused electrolyte. The metal, thus presented to the surface of the fused salt, could be caused to react with that fused salt by application of an electric current. The overall chemical reaction which has been caused to take place is:

$$4\ Na + UF_4 + 4\ F^* = U + 4\ NaF$$

$$F^* = \text{Faraday}$$

Although the postulated reaction between sodium metal and uranium tetrafluoride has been calculated to be spontaneous to temperatures as high as 2100°K., it is possible that the reaction is prevented from taking place because of insufficient physical contact between the sodium atoms and the UF_4 salt. A reduction reaction might actually take place at the interface of the two reactants but it is mechanically prevented from extending through the entire reactants mass. The electric current may actually only provide the means of obtaining the necessary intimate physical contact between reactants. The low voltages at which reduction could take place indicates that the reaction itself closely approaches a spontaneous process. The yields of uranium metal produced showed that the reaction was not violating Faraday's laws of electrolysis. The relatively poor yields of uranium metal may have been caused by an inherent design limitation of the test cell itself. Because of the close proximity of the anode to the cathode and the presence of both sodium metal and uranium metal in the operating cell, electric short circuits may have consumed portions of the current passed through the system. Some of the current may have passed through the cell by electrical means rather than by the electrolytic route. Another explanation for the low uranium yields is that the reaction is inefficient. In order to clarify this problem, later work on the system should employ larger electrochemical cells than the one described in this chapter. Larger electrochemical cells would be mechanically easier to operate and their results easier to correlate. A large cell would permit the anode to be positioned at different heights above the cathode floor. Operating the cell at different anode heights would allow more accurate determinations of voltage, amperage, and current efficiencies . Larger cells having greater quantities of electrolyte, would permit sampling of electrolyte during operation. Analysis of such samples would allow the course of the reaction to be followed. In the small cell used for this work, sampling of the electrolyte was not practical.

In addition to the reaction which was studied using the electrochemical device described in this chapter, other sluggish chemical reactions could also be studied in the same type of cell. Sodium or other metals could be caused to react with other fused salt systems to generate other useful products.

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APPENDIX

DETERMINATION OF OPTIMUM CONDITIONS

In a system, or in a chemical reaction which has several variables, it is difficult to determine the direction toward an optimum system or toward optimum reaction conditions unless experiments are designed to uncover that direction. Box and Wilson published a method by which it is possible to determine, with a minimum number of experiments, the direction toward optimum conditions.(4) Davies, in his text on the design and analysis of industrial experiments, treats the application of the Box-Wilson method to chemical reactions.(5) Essentially, the Box-Wilson method employs factorial designs as a means of developing an algebraic expression to relate the variables of a system to each other and to the outcome or yield. The equation which is developed is empirical. The method is not concerned with the reaction mechanisms or the chemical kinetics. Instead it treats only the gross relations of the system's operating variables to one another and to the yield of the process under study. Judgment must be exercised in the design of the experiment, in the selection of the limits of the operating variables, and in the interpretation of the results. Table 2 and Table 3 are examples of the determination of the directions toward optimum reaction conditions by the method of Box and Wilson. Table 2 contains a two-level, three-variable half-replica fractional factorial design. Table 3 contain a two-level five-variable quarter-replica fractional factorial design. Because the results of the design contained in Table 2 are more difficult to interpret than those in Table 3, the approach and calculations for the design in Table 3 are included in this appendix. Davies' text on design and analysis of experiments treats a simpler system as an example of approach and calculation and the reader is referred to the general case example given in that text for routine problems.(5).

The following information is contained in Table 2:

Factor	Factor Level	
U. conc. gms./liter (x_1)	30	50
HCl/UO_2Cl_2 moles/mole (x_2)	10	20
Residence time min./gm. (x_3)	5.0	6.42

The operation summary provides the following yield and factor level information for runs a, b, c, and d:

Run	Factor Level			Yield
	x_1	x_2	x_3	
a	-	-	-	88.3
b	+	+	-	78.7
c	+	-	+	92.0
d	-	+	+	65.9

The coefficients for the equation:

$$Y = b_o x_o + b_1 x_1 + b_2 x_2 + b_3 x_3$$

are calculated as follows:

$$b_o = (88.3 + 78.7 + 92.0 + 65.9)/4 = +81.2$$

$$b_1 = (-88.3 + 78.7 + 92.0 - 65.9)/4 = +4.1$$

$$b_2 = (-88.3 + 78.7 - 92.0 + 65.9)/4 = -8.9$$

$$b_3 = (-88.3 - 78.7 + 92.0 + 65.9)/4 = -2.3$$

For calculation of the path of steepest ascent:

	Factor		
	x_1	x_2	x_3
Base level	40	15	5.7
Unit	10	5	0.7
Unit xb	41	-44.5	-1.6

Examination of the equation with its coefficients shows that repetitive enlargements of the factors will not permit the yield to ever attain 100 per cent.

$$Y = 81.2 + 4.1x_1 - 8.9x_2 - 2.3x_3$$

But the information contained in this equation is useful in the design of the next factorial. It is noted that the average yield of the four trials was 81.2 per cent. The difference between 100 per cent and 81.2 per cent is 18.8 per cent. This difference represents the amount of yield improvement which the system is theoretically capable of obtaining by adjustment of the variables. It is noted that the positive coefficient of x_1 means that more concentrated uranium ion concentrations may be used in the test cell without reducing the yield of the uranous ion. An approximate calculation for the optimum uranium salt concentration may be obtained by multiplying the base level , 40, by 18.8/4, or 188 grams of uranium ion per liter of solution. Such a high concentration of uranium ion, from uranyl chloride, in solution would be too viscous for practical use. The negative coefficient for the x_2 term means that the system operates best with a minimum of hydrochloric acid. But, at least 4 moles of hydrochloric acid are required for each mole of uranyl chloride in solution, so the number of moles of HCl per mole of UO_2Cl_2 is listed as 4.

The negative coefficient for the x_3 term means that a short stay time in the cell will not diminish the yield of uranous product. This is dependent on the passage of sufficient amounts of electric current through the cell while the liquid is moving through the system. For the purpose of the first factorial design, the optimum residence time is approximated as 2.75 minutes per gram.

In practice, the experimenter will employ two or more factorial designs, each succeeding design based on information gathered from its predecessor. The sample shown in this appendix illustrates that the directions toward optimum reaction conditions can be simply established through factorial design. In this case an unknown system was experimented with in a series of four trial runs. At the completion of those four trials, the directions toward optimum reaction conditions were uncovered. On further examination of the system, the information gathered in the first four trials was used to set up more realistic factor levels.

BIOGRAPHICAL SKETCH

Donald Rae Allen was born April 13, 1927, at Staten Island, New York. In June, 1944, he was graduated from Curtis High School. During the second world war, he enlisted in and served with the United States Navy as a radio technician. In June, 1948, he received a Bachelor of Science degree from Wagner Memorial Lutheran College. In August, 1950, he received the Master of Arts degree from the University of Texas. He attended the University of Florida from April, 1951, to January, 1955. He has been professionally employed by the Dow Chemical Company, the Vitro Laboratories, and the Martin Company. He is a member of the American Chemical Society, the American Institute of Chemical Engineers, and the American Rocket Society.

This dissertation was prepared under the direction of the co-chairmen of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

February 1962

A H Gropp
Dean, College of Arts and
Sciences

Dean, Graduate School

Supervisory Committee:

E.E. Muschlitz, Jr.
Co-chairman

R.D. Dresdner
Co-chairman

Harry H. Sisler

A H Gropp

M.E. Tyler